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AMMONIA AND CARBON DIOXIDE HEAT PUMPS FOR HEAT RECOVERY IN INDUSTRY

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ABSTRACT

This paper presents a generic, numerical study of high temperature heat pumps for waste heat recovery in industry using ammonia and carbon dioxide as refrigerants. A study of compressors available on the market today, gives a possible application range of the heat pumps in terms of temperatures. Calculations of cycle performances are performed using a reference cycle for both ammonia and carbon dioxide as refrigerant. For each cycle a thorough sensitivity analysis reveals that the forward and return temperatures of the heat sink (condenser or gas cooler) of the heat pump are most important for the coefficient of performance, COP. By comparing the cycles it is found that for each set of operating conditions the two refrigerants perform equally well at one given inlet temperature of the heat sink. Above this temperature ammonia cycles have the best COP and below CO_2 cycles perform best. A general conclusion is that ammonia heat pumps are best at heat sink inlet temperatures above 28°C and CO_2 is best below 24°C, independent of other parameters.

1. INTRODUCTION

Waste heat recovery in industrial systems is a way of lowering the consumption of primary energy, primarily fossil fuels as oil and gas. By which means the waste heat can be recovered in the most effective way depends on the temperature level of the available heat. Ammar et al. (2012) define low grade waste heat as heat available at a temperature lower than the minimum temperature that could be utilized in the process by direct heat recovery. They propose vapour compression heat pumps as a viable option for heat recovery of low grade waste heat, where a heat source of 0-50°C should be upgraded to up to 90°C.

In many industrial processes (e.g. abattoirs, dairies) water in this temperature range is produced. In order to determine whether or not a heat pump would be beneficial for a given process, a screening of the total energy flows is necessary. Brondum et al. (2011) argue that both an energy optimisation and a consideration of the simultaneity of the waste heat production and the heat demand has to be conducted before the benefit of a heat pump for waste heat recovery can be evaluated. A pinch analysis should therefore be conducted before choosing a heat pump. If the pinch analysis shows that a heat pump is beneficial in a given process, the water upgraded by the vapour compression heat pump could be used either at some point in the production facility or it could be delivered to a district heating network and utilised elsewhere. However, hot water temperature requirements are one of the main challenges when using a vapour compression heat pump for the heat recovery, and in the present study we focus on heat pumps that produce water at minimum 60°C.

Ammonia and carbon dioxide are considered as refrigerants for heat pump applications in the present study as they are natural refrigerants with no ODP and no or low GWP. Several studies have considered using CO_2 as working fluid in heat pumps. Nekså (2002) and Austin and Sumathy (2011) give an overview of studies using CO_2 as refrigerant in different heat pump systems. Both of these review papers conclude that CO_2 has a good potential for water heating applications also at high temperatures, i.e. temperatures above 60°C.

The use of ammonia in heat pumps for water heating has until now not received as much focus in the published literature. One of the reasons is probably because ammonia is not suitable for domestic or other small scale applications due to toxicity and flammability and because most ammonia compressors have relatively low upper limits on the condensation temperatures, typically around 55°C. However, new high pressure compressors, where these limits are significantly higher, have entered the marked, such that it is possible to reach water temperatures above 60°C.

In this paper a comparison of CO_2 and NH_3 water heating heat pumps for temperatures above 60°C is presented. Firstly, a survey of available compressors is given. For different types of compressors application ranges are mapped and efficiencies are compared. Next, a reference cycle is chosen for each refrigerant. A sensitivity analysis shows, which parameter variations are affecting the coefficient of performance (COP) the most. Finally, an investigation of different combinations of evaporating temperature, water inlet temperature and water outlet temperature of the condenser/gas cooler is presented, and the performance of the two systems is compared for the different combinations.

The comparison of the systems is based on numerical modelling and is mainly a comparison of COP. A thermoeconomic comparison of similar heat pump systems was shown in Ommen et al. (2011).

2. COMPRESSOR SURVEY

A survey of available compressors was used to define the possible application ranges of different types of compressors for CO_2 and NH_3. Compressor maps were extracted from the Pack Calculation II software (Skovrup, 2011).

2.1 Carbon dioxide compressors

All CO_2 compressors that were identified as suitable for an industrial heat pump were semi-hermetic reciprocating compressors. The criteria for including a given compressor in the survey were that they have to be able to work transcritically, since water should be heated to at least 60°C. Furthermore, compressors were only included if evaporation above 0°C was a possibility. A total of 33 different compressors from three different manufacturers were included in the study. Figure 1 shows an overall application range of these compressors, meaning that at least one of the compressors is able to run at conditions within the outlined area. The reason why steps can be seen in the map is that this map is the union of the individual compressor maps.

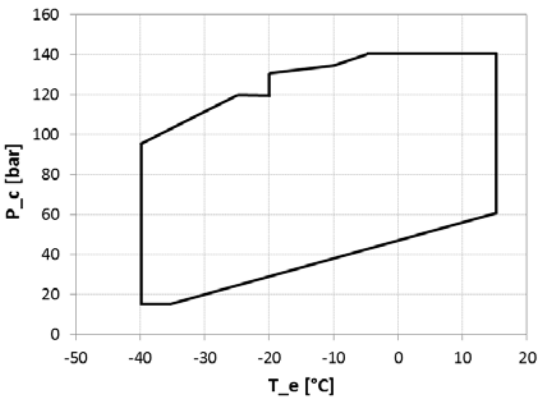

Figure 1: *Overall application range for the 33 different semi-hermetic reciprocating CO_2 compressors included in this study.*

2.2 Ammonia compressors

Ammonia compressors for industrial refrigeration systems are typically open type reciprocating or screw compressors. Most of these have an upper limit in condensation temperature of around 55°C, which means that these compressors can only heat a very limited water flow to a temperature above 60°C. However, these compressors could be used in the low stage of a two stage heat pump system. Figure 2 shows application ranges for 11 different open type screw compressors (blue), 6 different open type reciprocating compressors (yellow), two different high pressure reciprocating compressors (red), as presented by Korfitsen and

Kristensen (1998), and four single screw compressors (black). The reader should note the difference in ranges of the abscissae of Figures 1 and 2.

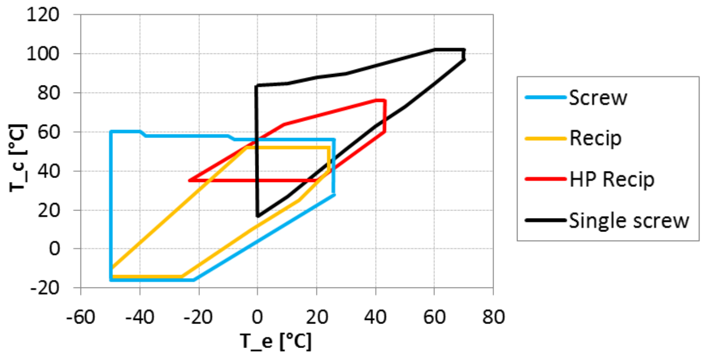

Figure 2: *Overall application range for 11 different open type screw compressors (blue), 6 different open type reciprocating compressors (yellow), two different high pressure reciprocating compressors (red) and four single screw compressors (black).*

2.3 Isentropic efficiencies

The isentropic efficiency of a specific compressor depends on the operating point, i.e. the pressure ratio, and can be calculated from compressor polynomials supplied by manufacturers. For the cycle calculations in the following section, a representative value of the isentropic efficiency for each compressor type is needed. We aim at a generic study and thus do not include performance data of one specific compressor into the reference systems. The values are chosen by studying the curves for isentropic efficiencies at different pressure ratios and different evaporation temperatures for the different compressor types and selecting the best possible isentropic efficiency for each type. This value will of course not be representative for a given system at varying working conditions, but represents a 'best case' performance for a system designed for the given conditions. A summary of the compressor survey, including the values for isentropic efficiencies, is shown in Table 1.

Table 1: *Summary of compressor parameters*

Compressor type	Max. P_c/T_c	Max. T_e [°C]	η	f_q
CO_2, semi-hermetic	140 bar	15	0,65	0,03
NH_3, open, recip.	55 °C	26	0,85	0,13
NH_3, open, high-pressure recip.	56-76 °C	43	0,85	0,08
NH_3, open, screw	58 °C	26	0,75	0,13
NH_3, open, single screw	82-102°C	70	0,88	0,26

3. SENSITIVITY ANALYSIS

3.1 Reference system

In order to determine which parameters affect the COP of heat pump the most, a sensitivity analysis is performed. The COP of the heat pump system is here defined as:

$$COP = \frac{\dot{Q}_H}{\dot{W}} \tag{1}$$

However, before the sensitivity analysis can be performed a reference cycle is set up, and a number of input parameters are chosen for modelling purpose. For the sensitivity analysis a simple one-stage system is chosen, and for this analysis the temperature limitations of the available compressors are not taken into account. In the following comparison between the two refrigerants (Section 4) different cycle configurations will be considered, and the limitations for the available compressors will also be taken into account.

It is assumed that the size of the system is given by the heating demand, thus the parameter fixing the system size is the mass flow rate of water to be heated. Furthermore the following parameters are considered as input to settle the states of the simple one-stage cycle:

- Water inlet temperature in the gas cooler/condenser ($T_{w,in}$)
- Water outlet temperature of the gas cooler/condenser ($T_{w,out}$)
- Evaporation temperature, (T_e)
- Superheat (*sh*)
- Pinch point temperature difference in gas cooler /condenser (ΔT_{pinch})
- Pressure loss in gas cooler/gas cooler section of the condenser (*PL*)
- Isentropic efficiency of the compressor (η)

The mass flow rate of water for the reference cycle is set to 1 kg/s and all the other parameter inputs are shown in Table 2**.**

Table 2: *Parameter input for reference cycle.*

Variable	$T_{w,out}$ [°C]	$T_{w,in}$ [°C]	T_e [°C]	sh [K]	ΔT_{pinch} [K]	PL [bar]	η [-]
Reference cycle	70	40	10	2	2	0	0,7

3.2 Condenser/gas cooler modelling

Neither a condensing temperature (ammonia) nor a gas cooler pressure (CO_2) is given as input parameter. The condensing temperature is determined by calculating the heat exchange between water and refrigerant in the three zones, desuperheating of gas, condensation and subcooling for a given pinch point temperature difference. In the reference cycle the same pinch point temperature is applied both at the point where the desuperheating and the condensing zones connect and at the outlet of the subcooling zone.

For the CO_2 gas cooler, the gas cooler outlet temperature is determined by a pinch point temperature difference. Apart from that the gas cooler pressure is fixed by optimization of the COP. This means that if the water inlet or outlet temperatures, or the mass flow rate of water change, the gas cooler pressure is changed to the pressure that will result in the highest COP at these conditions. Q-T diagrams of the heat transfer in the NH_3 condenser and the CO_2 gas cooler of the reference cycles are shown in Figure 3. The gas cooler pressure in the CO_2 cycle for the reference cycle is 110,3 bars.

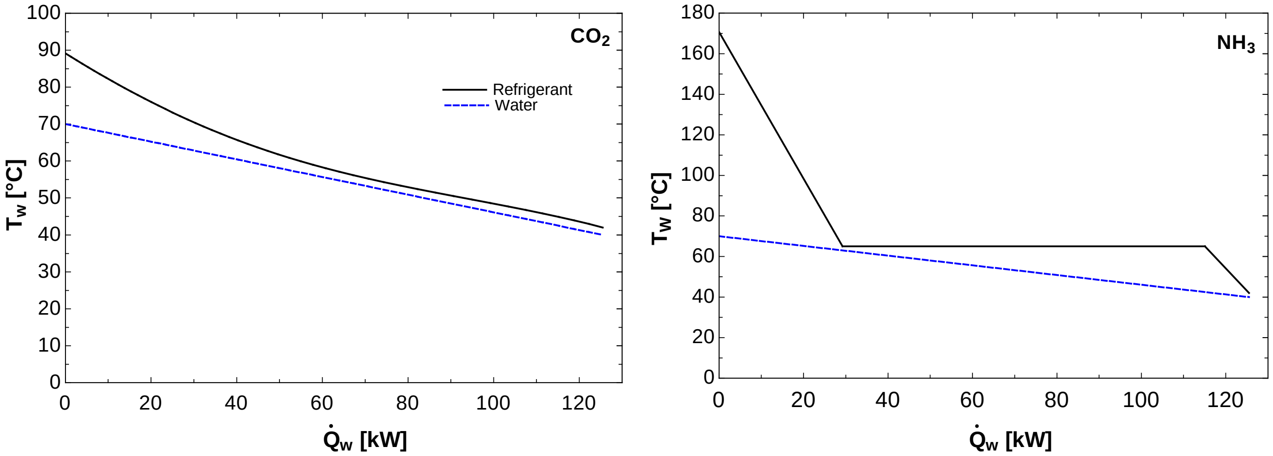

Figure 3: *Q-T diagrams of the CO_2 gas cooler (left) and the NH_3 condenser (right). The dashed, blue curve shows the water temperature and the solid, black curve shows the refrigerant temperature.*

3.3 Results of the sensitivity analysis

In order to perform the sensitivity analysis, the cycle input parameters shown in Table 2 are varied within reasonable intervals to determine how much a given parameter change affects the COP of the system. The considered intervals are shown in Table 3.

Table 3: *Intervals to be investigated for the different parameters.*

Variable	$T_{w,out}$ [°C]	$T_{w,in}$ [°C]	T_e [°C]	sh [K]	ΔT_{pinch} [K]	PL [bar]	η [-]
Reference cycle	[50;90]	[20;60]	[-10;30]	[0;20]	[0;8]	[0;4]	0,7

Figure 4 shows the results of the sensitivity study. The figure illustrates a relative change in COP as a function of a relative change in parameters. As mentioned, the variables are changed within the intervals indicated in Table 3, such that the relative change of a given parameter, which is shown on the abscissa of the figure, is related to these intervals. Each curve shows the full interval for a given parameter. On the ordinate a COP deviation of 0,1 corresponds to a change in COP of 10%.

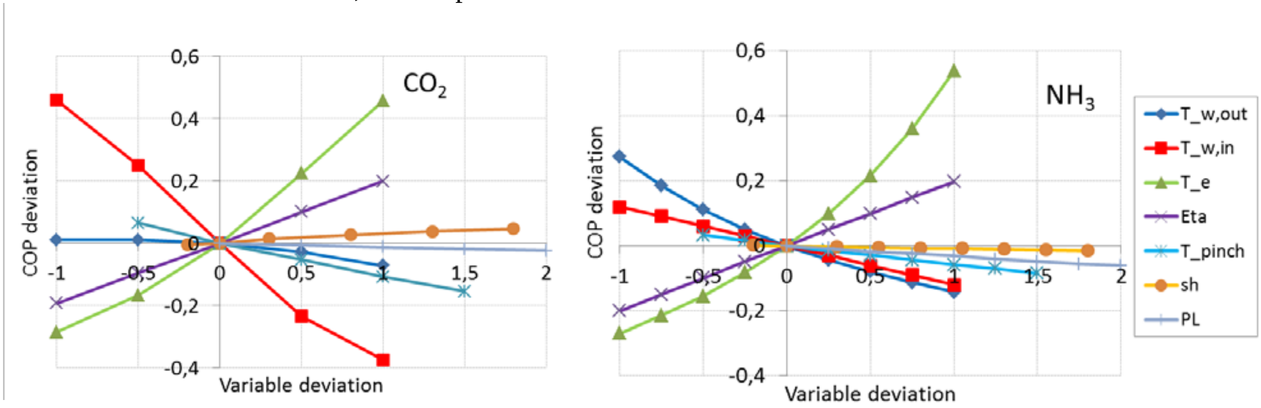

Figure 4: *Relative deviation in COP as a function of relative change in parameter variation.*

From Figure 4 it is evident that the different parameters affect the system performance differently and also that the influence of changing a given parameter on the COP is dependent on the refrigerant. For both refrigerants the evaporation temperature is a significant parameter, when optimizing the system performance. This is no surprise, since an increase of the evaporation temperature decreases the pressure ratio over the compressor. On the gas cooler/condenser side this is not as simple.

In the transcritical CO_2 system the COP is mainly affected by changing the water inlet temperature, while the water outlet temperature only has a minor impact on the COP. The water inlet temperature determines how low the gas cooler outlet temperature can be.

In an ammonia heat pump, changes in both the water inlet and the water outlet temperatures affect the COP significantly. This is because both of these temperatures will affect what the condensation temperature will be.

The isentropic efficiency of the compressor is equally important considering the two refrigerants. Furthermore, it is seen that pressure losses and superheat before the compressor does not affect the COP significantly.

4. COMPARISON OF CO_2 AND AMMONIA HEAT PUMPS

4.1 Idealized one-stage cycle heat pumps

The choice of refrigerant for a given heat pump application might depend on many factors. Safety, economy and energy efficiency are some of these fators. This study focusses on energy efficiency and the aim of this study is to determine at what general conditions an ammonia heat pump performs better than a CO_2 heat pump and vice versa. This means that here the COP is the only factor that is taken into consideration for the assessment.

From the sensitivity analysis it was found that mainly the evaporation temperature and the water supply and return temperatures affect the performance of the heat pump. With the mathematical model that was used for the sensitivity study, the COP is investigated as a function of the different temperatures. Figure 5 shows the COP of a simple one stage cycle using the reference cycle input parameters presented in Table 2 (apart from the temperatures, which are varied here), as a function of the water inlet temperatures. Curves are shown for different water outlet temperatures and for both NH_3 and CO_2. Furthermore results are shown for two different evaporation temperatures. The graphs show that for each desired water outlet temperature the curves for NH_3 and CO_2 intersect at some point. Meaning that for water inlet temperatures above this an NH_3 heat pump will have the highest COP while for lower water inlet temperatures the CO_2 heat pump will have the highest COP. From the two graphs in Figure 5 it is seen that this intersection is at water inlet temperatures between 20-28°.

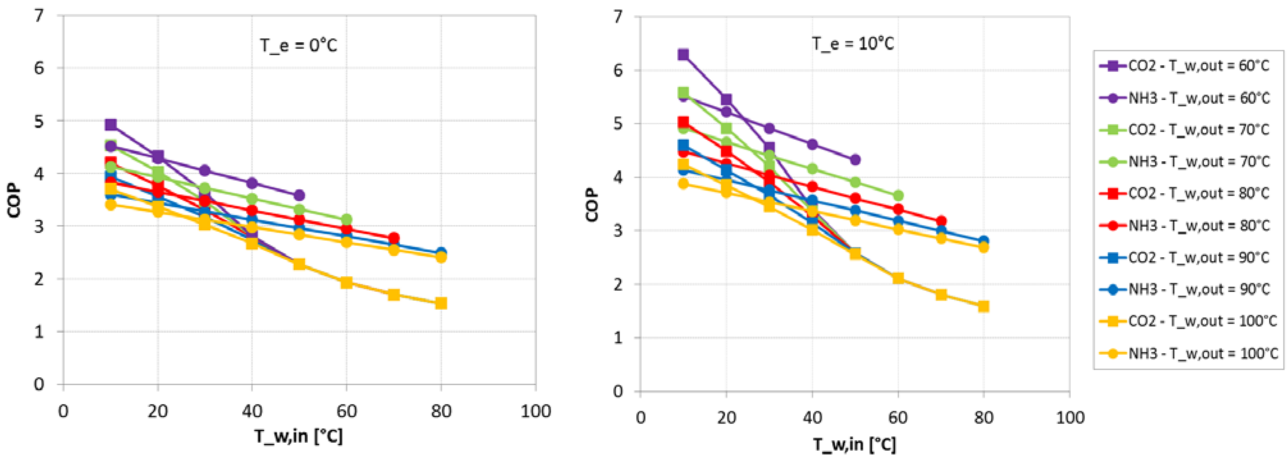

Figure 5: *COP as a function of water inlet temperature for different water outlet temperatures. Results for two different evaporation temperatures are presented, T_e = 0°C (left) and T_e = 10°C (right).*

In Figure 6 the intersection point at different combinations of the water temperature is shown for four different evaporation temperatures. For a given evaporation temperature the COP of a heat pump using CO_2 as refrigerant is highest for the combinations of water inlet and water outlet temperatures below the curve, whereas an NH_3 heat pump will have the highest COP for water temperature combinations above the curve.

It is seen that as a general rule, in heat pumps with a water inlet temperature above 28°C ammonia as the refrigerant will give the highest COP, where heat pumps with CO_2 are preferable at water inlet temperatures belov 20°C.

4.2 Practical heat pumps

The results presented above are all created on the basis of a simple one-stage cycle. However, limitations on available compressors and the possibility of using different cycle configurations, i.e. two-stage cycles may change the picture.

Therefore a number of different realistic solutions are set up. In the cycle models of these systems the general compressor limitations shown in section 2 are taken into account. For each compressor type the representative isentropic efficiency and heat loss factor from Table 1 are applied.

The different systems, which have been evaluated, are shown in the top of Figure 7. For CO_2 only a one-stage system is considered since no compressors are available for evaporation temperatures higher than 15°C, which makes it impossible to find a high stage compressor for a two-stage system. For NH_3 four different solutions have been investigated.

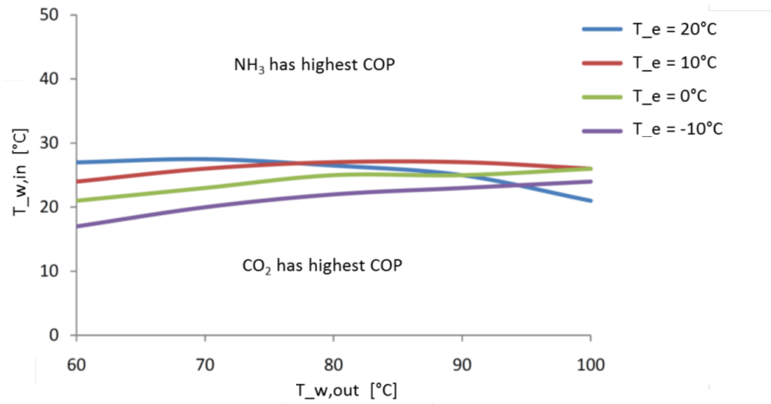

Figure 6: *The curves show at which combination of water inlet and water outlet temperatures the COP of a NH_3 and a CO_2 heat pump are equal.*

- One-stage CO_2
- One-stage NH_3 with a high pressure reciprocating compressor
- One-stage NH_3 with a single screw compressor and oil cooling
- Two-stage NH_3 with a reciprocating compressor at low stage and a single screw compressor at high stage, open intercooler
- Two-stage NH_3 with a reciprocating compressor at low stage and a high pressure reciprocating compressor at high stage, open intercooler

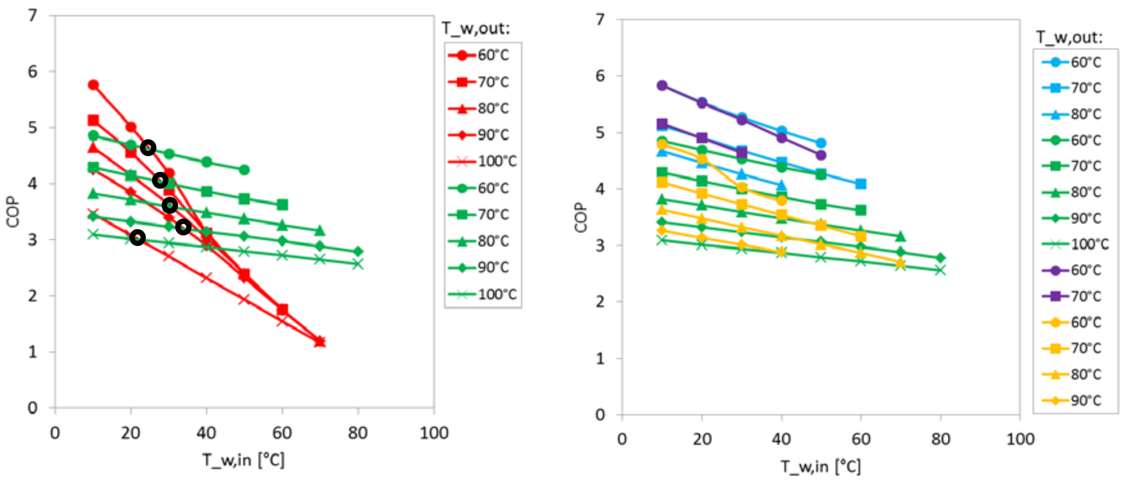

Figure 7: Left: *Comparison of COP of one NH_3 system and one CO_2 system at T_e = 10°C for different water outlet temperatures. The black circles mark the crossing points of the CO_2 and NH_3 systems at equal water outlet temperatures.* Right: *Comparison of the performance of the four different NH_3 systems at different water outlet temperatures and T_e = 10°C.*

In Figure 7 one colour is assigned for each technology. The graphs show the COP as a function of the water inlet temperature for different water outlet temperatures. In the left part of the figure the single stage CO_2 system is compared to the two-stage NH_3 system with a reciprocating compressor in the low stage and a single screw in the high stage. It is seen that also here the CO_2 system performs best at low water inlet temperatures and the NH_3 system performs best at high water inlet temperatures. However, the cross-over (marked with black circles) is not within a band as narrow as for the idealized case. The right graph of Figure 7 shows a comparison of the four different NH_3 systems and it is seen that two of the systems actually perform equally well as the CO_2 system at low water inlet temperatures. Another way of illustrating similar results using tables is shown in Brondum et al. (2011) and Reinholdt et al. (2012).

The conclusions drawn from the general systems with no practical limitations are hence partly supported by the analysis shown in Figure 7, but also partly disclaimed since it also depends on the system configuration and other parameters, which solution is performing best.

5. CONCLUSIONS

This paper presents a comparison of ammonia and carbon dioxide heat pumps for heat recovery in industry. A survey of the compressor market has been performed and general compressor maps for different types of compressors were shown. A thorough sensitivity analysis, based on mathematical models of simple one-stage heat pump systems showed that evaporation temperature, water inlet and water outlet temperatures in the compressor/gas cooler are the parameters primarily affecting the COP of the heat pump systems. Next a general comparison of the two working fluids was performed, and it was shown that the CO_2 heat pump has a higher COP than the NH_3 heat pump for water inlet temperatures below 20°C. For water inlet temperatures above 28°C NH_3 heat pumps gave the highest COP. Furthermore five different more realistic systems were studied and it was shown that the general results obtained from the simple system were less significant. The range of water inlet temperatures for which one of the refrigerants is superior is less pronounced for practical situations.

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NOMENCLATURE

η	isentropic efficiency (-)
f_q	heat loss factor (-)
P	pressure (bar)
PL	pressure loss (bar)
sh	superheat (K)
T	temperature (°C)
$\dot{Q}$	heat flow rate (kW)
$\dot{W}$	compressor power (kW)

Subscripts

e	evaporation/evaporator
H	hot stream
in	inlet
out	outlet
w	water

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